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TITLE: Heteropoly acids supported on polyoxometallate salts and their preparation

BSPL:

where G is Cu.sup.++ or Fe.sup.+++ or an oxy ion of Ti, V, Cr, U, As, Bi, Sb, Nb or La, or is absent; X is a Group IIIB, IVB, VB, VIB or transition element,

such as phosphorus, silicon, gallium, aluminum, arsenic, germanium, boron,

cobalt, cerium, praseodymium, uranium and thorium; M is molybdenum or tungsten,

or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', such as titanium, zirconium, hafnium,

vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese,

rhodium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium,

platinum, copper, zinc or combination thereof, z' is the charge on said cation G; k' is 1 to 5, m' is 5 to 17, x' is 0 to 3, n is 0 to 3; y' is 18 to 60; when M is molybdenum, x' is 0 to 3; when M is tungsten, x' is 0 to 6; and e' is the charge of the anion of the polyoxometallate. When M is a combination of molybdenum and tungsten, x' is preferably 0. The support component comprises

an insoluble polyoxometallate salt having the formula:

DEPL:

where cation G is Cu.sup.++ or Fe.sup.+++ or an oxy ion of Ti, V, Cr, U, As, Bi, Sb, Nb or La, or is absent; X is a Group IIIB, IVB, VB, VIB or transition element, such as phosphorus, silicon, gallium, aluminum, arsenic, germanium,

boron, cobalt, cerium, praseodymium, uranium and thorium; M is molybdenum or

tungsten, or combinations thereof, M' is vanadium; M'' is independently zinc or

a transition metal different from M and M', such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, zinc or combination thereof; z' is the charge on said cation G; k' is 1 to 5, m' is 5 to 17, n is 0 to 3; y' is 18 to 60; when M is molybdenum, x' is 0 to 3; when M is tungsten, x' is 0 to 6; and e' is the charge of the anion of the polyoxometallate. When M is a combination of molybdenum and tungsten, x' is preferably 0.

DEPL:

where, in the HPA $H_{(e'-bz')} G_b (X_{k'} M_{m'-x'} M'_{x'} M''_{n'} O_{y'})_{-e'}$, G, the cation, is Cu^{++} or Fe^{+++} , or an oxy ion of titanium (Ti), vanadium (V), chromium (Cr), uranium (U), arsenic (As), bismuth (Bi), tin (Sb), niobium (Nb), or lanthanum (La), or is absent; X, the central or hetero atom, is a Group IIIB, IVB, VB, VIB or **transition element, such as phosphorus, silicon, gallium**, aluminum, arsenic, germanium, boron, cobalt, cerium, praseodymium, uranium and thorium; M, the first framework metal is molybdenum or tungsten or combinations thereof; M' is vanadium substituted for first framework metal M; M'', the second framework metal, is different from M and is independently zinc or a transition metal, such as titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, zinc or combination thereof; k' is 1 to 5; m' is 5 to 17; n' is 0 to 3; y' is 18 to 59; when M is molybdenum, x' is 0 to 3; and when M is tungsten, x' is 0 to 6; e' is the charge of the anion of the heteropolyacid; and z' is the charge on the cation G; and where, in the POM $C_a H_{(e'-bz')} (X_{k'} M_{m'-x'} M'_{x'} M''_{n'} O_{y'})_{-e'}$, C is selected from the group consisting of potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum, ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof; X is a Group

IIIB, IVB, VB, VIB or transition metal; M is molybdenum or tungsten or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', or combination thereof; z is the charge on said cation C; k is 1 to 5, m is 5 to 17, n is 0 to 3; y is 18 to 60; when M is molybdenum, x is 0 to 3; and when M is tungsten, x is 0 to 6; and when "az" equals "e", there are no protons present in the polyoxometallate support. Preferably, when M is a combination of molybdenum and tungsten, x is 0.